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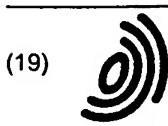
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(54) **Oxide coated cutting tool**

(57) According to the present invention there is provided a body at least partially coated with one or more refractory layers of which at least one layer essentially consist of α - Al_2O_3 . Said α - Al_2O_3 -layer consists of essentially equiaxed grains with an average grain size of $< 1 \mu\text{m}$ and with a bimodal grain size distribution with

coarser grains with an average grainsize in the interval $0.5 - 1 \mu\text{m}$ and finer grains with an average grainsize of $< 0.5 \mu\text{m}$. The Al_2O_3 -layer further contains striated zones containing titanium ($> 5 \text{ at } \%$) but no nitrogen or carbon. This particular microstructure is obtained by temporarily stopping the gases needed for the growth of the Al_2O_3 -layer and introducing TiCl_4 .

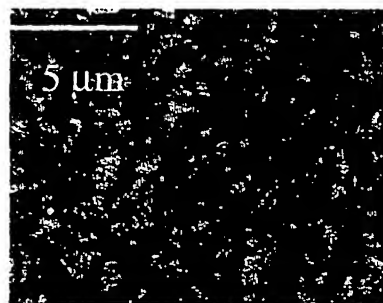


Fig. 1a (invention)

Striated
zones

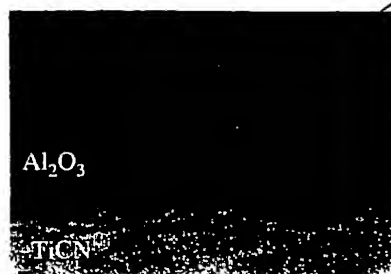


Fig. 1b (invention)

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Description

[0001] The present invention relates to a coated cutting tool for chipforming machining. The coating includes at least one alumina (Al_2O_3) layer characterized by fine, equiaxed grains.

[0002] Cemented carbide cutting tools coated with various types of Al_2O_3 -layers using Chemical Vapour Deposition (CVD), e.g., pure κ - Al_2O_3 , mixtures of κ - and α - Al_2O_3 coarse grained α - Al_2O_3 and fine grained textured α - Al_2O_3 have been commercially available for years generally in multilayer combinations with other metal carbide and/or nitride-layers, the metal being selected from transition metals of the IVB, VB and VIB groups of the Periodic Table.

[0003] Al_2O_3 crystallises in several different phases: α , κ , γ , δ , θ etc. The two most frequently occurring phases of CVD-produced wear resistant Al_2O_3 -layers are the thermodynamically stable, α -phase and the metastable κ -phase or a mixture thereof. Generally, the κ -phase exhibits a grainsize in the range 0.5-3.0 μm and the grains predominately grow through the whole coating forming a columnar type coating morphology. Furthermore, the κ - Al_2O_3 -layers are free from crystallographic defects and also free from micropores and voids.

[0004] Coarsegrained (3-6 μm) α - Al_2O_3 often possesses porosity and crystallographic defects, while finegrained textured α - Al_2O_3 are free of defects with very pronounced columnar-shaped grains.

[0005] In US 5,674,564 is disclosed a method of growing a finegrained κ -alumina-layer by employing a low deposition temperature and a high concentration of a sulphur dopant.

[0006] In US 5,487,625 a method is disclosed for obtaining a fine grained, (012)-textured α - Al_2O_3 -layer consisting of columnar grains with a small cross section (about 1 μm).

[0007] In US 5,766,782 a method is disclosed for obtaining a finegrained (104)-textured α - Al_2O_3 -layer.

[0008] As mentioned above, all Al_2O_3 -layers produced by the CVD technique possess a more or less columnarlike grainstructure. An Al_2O_3 -layer with an equiaxed grainstructure is, however, expected to show some favourable mechanical properties, e.g. resistance to crack propagation, as compared to a layer with a columnar grainstructure. One well-known and possible technique to avoid columnar grain growth is to deposit a so-called multilayer structure in which the columnar growth of e.g. Al_2O_3 is periodically interrupted by the growth of a thin, 0.1-1 μm second layer such as disclosed in US 4,984,940. The second layer should preferably have a different crystal structure or at least different lattice spacings in order to be able to initiate renucleation of the first layer. One example of such a technique is when the Al_2O_3 growth periodically is interrupted by a short TiN deposition process resulting in a $(\text{Al}_2\text{O}_3+\text{TiN})_x$ multilayer structure with a thickness of the individual TiN-layers of about 0.1-1 μm e.g. see Proceedings of the 12:th European CVD Conference page pr.8-349. However, such multilayer structures very often suffer from a low adherence between the two different types of layers.

[0009] It is the object of the present invention to provide onto a hard substrate, or preferably onto a hard substrate coated with a $\text{TiC}_x\text{N}_y\text{O}_z$ -layer, at least one single phase α - Al_2O_3 -layer with a microstructure which is different from the prior art columnar α - or κ - Al_2O_3 CVD layers mentioned above. It is also the object of the present invention to provide a high performance tool coating comprising the invented Al_2O_3 -layer.

[0010] It is a further object of the invention to provide an alumina coated cutting tool insert with improved cutting performance in steel, stainless steel, cast iron and in particular nodular cast iron.

[0011] Figure 1a is a Scanning Electron Microscope (SEM) micrograph of an Al_2O_3 -layer according to the present invention.

[0012] Figure 1b is a SEM micrograph at high magnification of a polished cross-section of an Al_2O_3 -layer according to the present invention.

[0013] Figure 2a is a SEM micrograph prior art Al_2O_3 -layer.

[0014] Figure 2b is a SEM micrograph at high magnification of a polished cross-section of an Al_2O_3 -layer according to the prior art.

[0015] Figure 3a is a SEM micrograph of a prior art multilayer $\text{Al}_2\text{O}_3/\text{TiN}$ coating.

[0016] Figure 3b is a SEM micrograph at high magnification of a polished cross-section of an $\text{Al}_2\text{O}_3/\text{TiN}$ multilayer according to the prior art.

[0017] Surprisingly it has been found that a non-columnar α - Al_2O_3 -layer can be deposited by interrupting the Al_2O_3 growth process by obstructing the flow of the CO_2 , AlCl_3 , HCl and H_2S gases to the reactor chamber and then immediately introducing TiCl_4 (H_2 is already present in the reactor) for a short period of time. When the reactant gases AlCl_3 , HCl , CO_2 and H_2S are allowed to reenter the reactor again in that mentioned order, renucleation of Al_2O_3 will take place. The duration of the TiCl_4 treatment as well as the TiCl_4 concentration are important parameters which must be optimized in order to obtain the desired result. If the TiCl_4 concentration is too low or/and treatment time is too short, the renucleation of the Al_2O_3 -layer will not be sufficiently dense to cover a sufficient portion of the whole coating surface. If, on the other hand, the TiCl_4 concentration is too high and/or the treatment time is too long, the cohesion between the Al_2O_3 grains will be too weak resulting in a low quality coating.

[0018] The method of the present invention thus relates to the coating of a body with an α -alumina-layer during which the body is brought in contact with a hydrogen carrier gas containing one or more halides of aluminium and a hydrolysing

and/or oxidising agent at temperature of the body between 950 and 1000 °C. The oxidation potential of the CVD-reactor atmosphere prior to the nucleation of Al_2O_3 is kept at a low level keeping the total concentration of H_2O , water vapour, or other oxidising species, preferably less than 5 ppm. The Al_2O_3 growth is started by sequencing the following gases AlCl_3 , HCl and CO_2 (H_2 is already present in the reactor) into the reaction chamber in that mentioned order or by using the start-up procedures described in any of the prior art patents, US 5,487,625 and US 5,766,782, in order to achieve different textures of the Al_2O_3 -layer. After 10-60 minutes a sulphur dopant, preferably H_2S , is added to the gas mixture. The flow of the CO_2 , AlCl_3 , HCl gases and the sulphur dopant are periodically interrupted at intervals of 10-50 minutes and 1-10 % (of the hydrogen flow) TiCl_4 is allowed to enter the reactor for a period of 1-10 minutes and then again replaced by AlCl_3 , HCl , CO_2 and the sulphur dopant in that mentioned order. This procedure is repeatedly carried out in order to obtain a striated, bimodal $\alpha\text{-Al}_2\text{O}_3$ -layer-structure with the desired grainsize and texture.

[0019] In contrast to the columnar grains of prior art Al_2O_3 -layers, the grains of the Al_2O_3 -layers according to the present invention are essentially equiaxed with a bimodal structure which is a mixture of small and large grains. The obtained grainsize and the distribution of the same are dependent on the number of TiCl_4 treatments carried out. The more frequently the Al_2O_3 process is interrupted and the Al_2O_3 surface is treated with TiCl_4 , the smaller the Al_2O_3 grains will be. The coarser Al_2O_3 grains have an average grain size $d_c \leq 1 \mu\text{m}$ and the finer Al_2O_3 grains $0.1 \leq d_c \leq 0.3 \mu\text{m}$.

[0020] The grainsize in the $\alpha\text{-Al}_2\text{O}_3$ -layer can be determined from a SEM top-view micrograph at about 4000X magnification. Such a micrograph of an Al_2O_3 -layer surface according to the present invention is shown in Fig 1a. In Fig 2a and 3a, the micrographs of prior art Al_2O_3 -layers are shown. The size and the shape of the grains can easily be observed. Furthermore, the striated zones in the $\alpha\text{-Al}_2\text{O}_3$ -layer which contain titanium and oxygen are visible in a polished cross section at 4000-6000 X magnification. These striated zones which do not contain any carbon or nitrogen may also contain some aluminium. The striated zones are preferably $< 0.2 \mu\text{m}$ thick and the number of striated zones per μm Al_2O_3 -layer should be 1-10. They may be closely linked together but in some cases almost resembling a multilayer structure. The presence of these striated zones in the Al_2O_3 structure evidently limits the Al_2O_3 grain growth and makes renucleation possible without the negative effect of fully intermediate or intervening layers.

[0021] By selecting appropriate conditions for the initial growth of the Al_2O_3 -layer, e.g. according to the procedures in patents US 5,487,625 and US 5,766,782, Al_2O_3 -layers textured in the (012)-, (024)- or (104)-directions with a texture coefficient $\text{TC} > 1.3$ can be deposited.

[0022] The texture Coefficient, TC, is defined as:

$$\text{TC}(\text{hkl}) = \frac{I(\text{hkl})}{I_o(\text{hkl})} \left\{ \frac{1}{n} \sum \frac{I(\text{hkl})}{I_o(\text{hkl})} \right\}^{-1}$$

where

$I(\text{hkl})$ = measured intensity of the (hkl) reflection

$I_o(\text{hkl})$ = standard intensity of the ASTM standard powder pattern diffraction data

n = number of reflections used in the calculation, (hkl) reflections used are: (012), (104), (110), (113), (024), (116)

[0023] More specifically, the coated body comprises a cutting tool with a substrate of cemented carbide, cermet, ceramic or superhard material and with at least on the functioning parts of the surface thereof a coating consisting of a hard wear resistant material. In said coating at least one layer is a single phase $\alpha\text{-Al}_2\text{O}_3$ -layer according to the present invention, and said single phase $\alpha\text{-Al}_2\text{O}_3$ -layer having a thickness in the range 0.5-25 μm . The other layers in the coating structure may be TiC or related carbide, nitride, carbonitride, oxycarbide and oxycarbonitride of a metal selected from the Groups IVB, VB, and VIB of the Periodic Table, the elements B, Al and Si and/or mixtures thereof. Such other layers may be deposited by CVD, PACVD (Plasma CVD), PVD (Physical Vapour Deposition) or MT-CVD (Moderate Temperature CVD). At least one of such other layers is in contact with the substrate. The total thickness of the coating of the cutting tool can vary between 1 and 30 μm .

Example

[0024]

A) Cemented carbide cutting inserts in style CNMG 120412-KM with the composition 6 weight-% Co and balance WC were coated with a 5 μm thick layer of $\text{Ti}(\text{C},\text{N})$ using the MTCVD-technique with TiCl_4 , H_2 , N_2 and CH_3CN as process gases. In subsequent process steps during the same coating cycle, a 0.5 μm $\text{TiC}_x\text{N}_y\text{O}_z$ -layer with an approximate composition corresponding to $x=0.5$, $y=0.3$ and $z=0.2$ was deposited followed by a 6 μm thick layer of $\alpha\text{-Al}_2\text{O}_3$ deposited according to the invented coating process. Prior to the nucleation of the Al_2O_3 the oxidation

potential of the carrier gas H_2 (only gas present in the reactor) i.e. the water vapour concentration, was explicitly set to a low level, less than 5 ppm.

Then the first Al_2O_3 -layer step 1 was started up. The process conditions during the Al_2O_3 deposition were as below:

Step	1	2	3	4
CO_2	4%	4%	0%	4%
$AlCl_3$	4%	4%	0%	4%
H_2S	-	0.2%	0%	0.2%
HCl	1.5%	5%	0%	5%
H_2	balance	balance	balance	balance
$TiCl_4$	-	-	5%	-
Pressure	60 mbar	60 mbar	60 mbar	60 mbar
Temperature	1000°C	1000°C	1000°C	1000°C
Duration	30 min	20 min	5 min	20 min

The Al_2O_3 -layer was deposited by proceeding through step 1, 2 and 3 and then looping between step 3 and step 2 nine times and finishing the process by step 4. Hence, the Al_2O_3 -process was interrupted and treated with $TiCl_4/H_2$ altogether ten times.

XRD-analysis of the deposited $\alpha-Al_2O_3$ showed a strongly textured structure with a texture coefficient $TC(012)$ of 1.7 of the (012) planes and $TC(024)$ of 1.5 of the (024) planes.

From the SEM-micrographs taken from the top surface, similar to Fig 1a, the grainsize was determined. The coarse grains had an average grainsize of 0.9 μm and the fine grains had an average grainsize of 0.3 μm .

B) The cemented carbide substrate of A) was coated with $Ti(C,N)$ (5 μm), a 0.5 μm $TiC_xN_yO_z$ -layer and Al_2O_3 (6 μm) as set forth in A) except for that the Al_2O_3 process was carried out according to prior art technique i.e. the same process as described under A) except for that the $TiCl_4/H_2$ -treatments were excluded and an Al_2O_3 process time of 290 min. This resulted in an Al_2O_3 -layer consisting essentially of the $\kappa-Al_2O_3$ phase with an average grain-size of about 2 μm , Fig 2a.

C) The cemented carbide substrate of A) was coated with $Ti(C,N)$ (5 μm), a 0.5 μm $TiC_xN_yO_z$ -layer and a 6 μm of multilayered Al_2O_3 coating on top as set forth in A) except for that step 3 was substituted by a prior art TiN-process step. The process parameters for this TiN-step were as follow: 2 % $TiCl_4$, 40 % N_2 , 58 % H_2 and a process time of 3 min. This resulted in a multilayer coating consisting of eleven layers of Al_2O_3 and ten thin layers of TiN. The Al_2O_3 -layer was determined to consist of the κ -phase.

[0025] Coated tool inserts from A), B) and C) were all wet blasted with 150 mesh Al_2O_3 powder in order to smooth the coating surfaces.

[0026] The cutting inserts were then tested with respect to edge line and rake face flaking in a facing operation in nodular cast iron. The shape of the machined work piece was such that the cutting edge is intermitted twice during each revolution.

Cutting data:

Speed = 170 m/min,

Cutting depth = 2.0 mm and

Feed = 0.1 mm/rev.

[0027] The inserts were run one cut over the face of the work piece. This test is very decisive and demanding when cutting nodular cast iron.

[0028] The percentage of the edge line in cut that obtained flaking into the carbide substrate was recorded for each insert tested as well as to what extent flaking occurred on the rake phase of the cutting insert.

[0029] The results are expressed in the table below as an average value of the four inserts.

		Flaking	
		Edge line	Rake face
A)	$\alpha-Al_2O_3$ single phase/striated (acc. to invention)	0 %	only spot-wise flaking of the Al_2O_3 -layer

(continued)

		Flaking	
		Edge line	Rake face
5	B) κ -Al ₂ O ₃ (prior art)	90 %	severe Al ₂ O ₃ -flaking
10	C) multilayer Al ₂ O ₃ /TiN (prior art)	70 %	Flaking between TiN and Al ₂ O ₃ layers

Claims

1. Cutting tool comprising a body on which at least on the functioning parts of the surface thereof, a hard and wear resistant coating is applied **characterized** in said coating comprising a structure of one or more refractory layers of which at least one layer essentially consist of α -Al₂O₃ in that said α -Al₂O₃-layer consists of essentially equiaxed grains with an average grainsize of <1 μ m and further containing striated zones containing >5 at % titanium but no nitrogen or carbon.
2. Cutting tool according to claim 1 **characterised in that** said Al₂O₃-layer has a bimodal grainsize distribution with coarser grains with an average grain size $d_c \leq 1 \mu$ m and the finer grains d_f in the interval $0.1 \leq d_f \leq d_c/3$.
3. Cutting tool according to any of the preceding claims **characterised in that** said striated zones are <0.2 μ m thick and the number thereof per μ m Al₂O₃-layer 1-10.
4. Cutting tool according to any of the preceding claims **characterized in that** said alumina layer is textured in at least one of the directions (012), (104) or (024) with a texture coefficient larger than 1.3, the texture coefficient being defined as:

$$TC(hkl) = \frac{I(hkl)}{I_o(hkl)} \left\{ \frac{1}{n} \sum \frac{I(hkl)}{I_o(hkl)} \right\}^{-1}$$

where

$I(hkl)$ = measured intensity of the (hkl) reflection

$I_o(hkl)$ = standard intensity of the ASTM standard powder pattern diffraction data

n = number of reflections used in the calculation

(hkl) reflections used are: (012), (104), (110), (113), (024), (116).

5. Cutting tool according to any of the preceding claims **characterized in having** at least one layer in contact with the substrate, said layer comprising of a nitride, carbide, carbonitride, oxycarbide and/or oxycarbonitride of a metal selected from the Groups IVB, VB and VIB of the Periodic Table, B, Al, and Si and/or mixtures thereof.
6. Method of coating a body with an α -alumina layer at which the body is brought in contact with a hydrogen carrier gas containing one or more halides of aluminium and a hydrolysing and/or oxidising agent at 950-1000 °C wherein the oxidation potential of the CVD-reactor atmosphere prior to the nucleation of Al₂O₃ is kept at a low level using a total concentration of H₂O or other oxidising species preferably below 5 ppm, the Al₂O₃ growth being started up by entering the following gases into the reaction chamber: AlCl₃, HCl and CO₂ and after 20-60 min a sulphur dopant, preferably H₂S, is added **characterized in that** during the growth, the CO₂, AlCl₃, HCl and the sulphur dopant are repeatedly stopped with intervals of 10-50 min and TiCl₄ is allowed to enter the reactor for 1-10 min in a concentration of 1-10% then replaced by AlCl₃, HCl, CO₂ and the sulphur dopant in the mentioned order.



Fig. 2a (prior art)

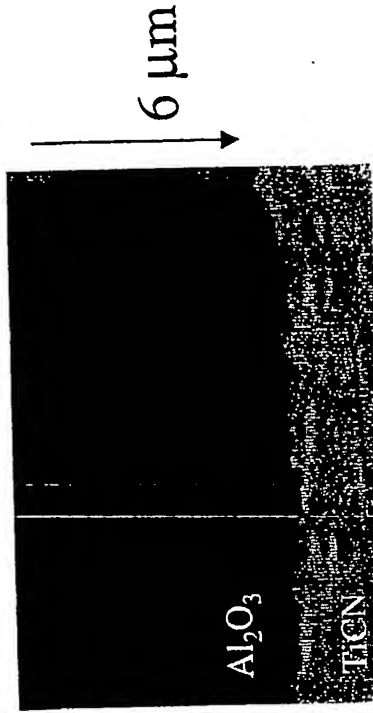
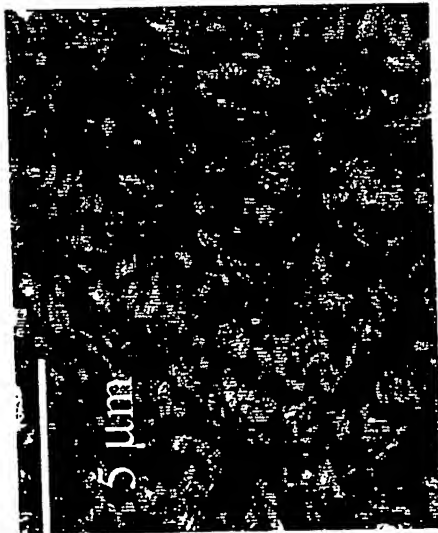


Fig. 2b (prior art)



Striated
zones

Fig. 1a (invention)

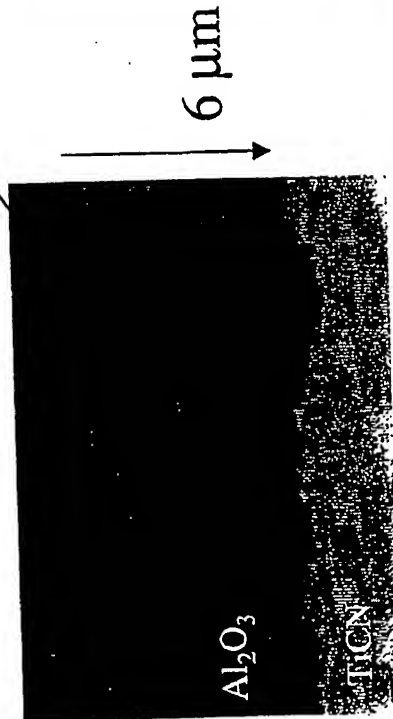


Fig. 1b (invention)

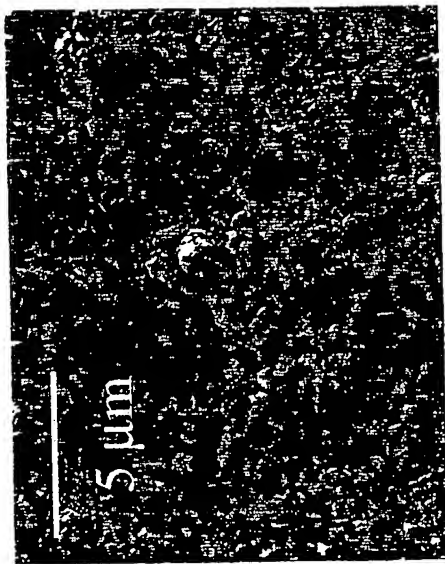


Fig. 3a (prior art)

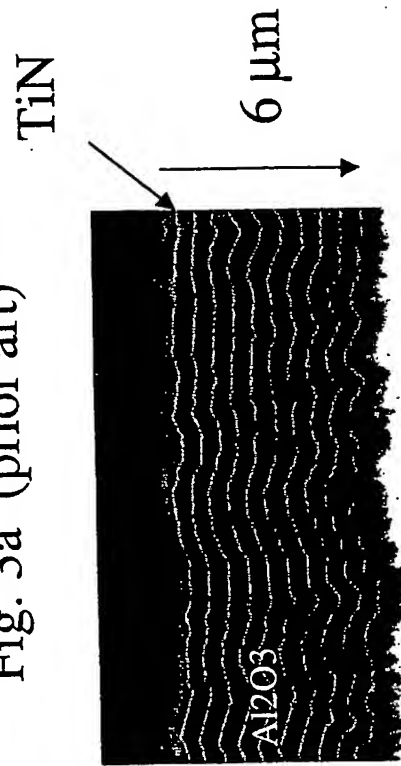


Fig. 3b (prior art)